

DEVELOPMENT OF MATERIAL SPECIFICATIONS
AND QUALIFICATIONS OF POLYMERIC MATERIALS
FOR THE JPL SPACECRAFT MATERIALS GUIDEBOOK
II. RTV SILICONE ADHESIVES
AND POTTING COMPOUNDS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950745
UNDER NASA CONTRACT NO. NAS7-100

JPL COGNIZANT ENGINEER: HUGH MAXWELL

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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SRI Project PRD-5046

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SUMMARY

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Five RTV* silicone potting compounds and four RTV* silicone adhesive/sealants were selected by JPL cognizant engineer H. Maxwell for study under simulated space conditions. Outgassing characteristics of these materials were determined at 150°C and 5×10^{-6} mm Hg. Outgassed condensable materials were analyzed by infrared spectroscopy; and any visual changes such as sample darkening and softening were noted. Under these conditions, each RTV silicone material evolved large amounts of condensable oil, although the appearance and properties of the test specimens remained unchanged. The oil was identified by infrared spectroscopy as low molecular weight silicone oils of the same chemical type as the RTV compound itself.

Because of the undesirability of the oil, various modified preparatory procedures were investigated. Use of larger amounts of curing agent in formulating the silicone test specimens was totally ineffective: Weight loss characteristics were very nearly the same as those for the unmodified material, and large amounts of oil were evolved. Postcuring the resins in a forced draft oven for 24 hours at 150°C was only partially successful: Weight losses were approximately halved and some oil evolution took place. Finally, postcuring of the materials at 150°C for 24 hours at 10^{-4} mm Hg was found to be completely successful, inasmuch as the oil was eliminated and weight losses were greatly reduced. *Author*

*Trademark for General Electric Company's room temperature vulcanizing silicone rubbers.

INTRODUCTION

The over-all objective of this program is to provide assistance to the JPL staff members in the development of specifications and procedures for polymeric spacecraft materials. This includes definitions of properties, tests, and environments which are sensitive and meaningful, and collection of pertinent property, environmental, and materials data for use in specifications. Of particular importance to this program are the outgassing characteristics of various polymeric materials under thermal vacuum conditions. The classes of materials to be examined were selected by the JPL cognizant engineers. The first class of materials examined were the epoxide adhesives.¹ The second class of selected materials--the subject of this report--are the general purpose silicone rubbers used as potting and adhesive compounds, specifically, the Room Temperature Vulcanizing (RTV) compounds of the General Electric Company. Samples were prepared and cured using procedures recommended by GE and their weight loss characteristics were determined at 150°C and 10⁻⁶ mm Hg. This temperature (150°C) approximates the temperature currently recommended for the sterilization of spacecraft. In addition, the volatile condensable oils were analyzed to determine their source (i.e., additives, chain degradation, etc.) so that improvements in the materials or in their processing conditions could be recommended.

¹Development of Material Specifications and Qualifications of Polymeric Materials for the JPL Spacecraft Materials Guidebook, Special Report No. I. Epoxide Adhesives.

EXPERIMENTAL

Materials

RTV silicones 11, 60, 511, 560, 615, 102, 106, 108, and 112 were obtained from Mr. Red Baurmeister, Silicone Products Department, General Electric Company, 1201 Bryant Street, San Francisco. All materials were stored under refrigeration to minimize side reactions. The potting compounds are liquids or pastes which cure on addition of a catalyst to form the solid rubber. The catalyst used for all potting compounds (except RTV-615 which is supplied with its own catalyst) was Thermolite-12 (T-12) which is dibutyl tin dilaurate. The composition of these compounds, as well as the weights and surface areas of the corresponding test specimens, are summarized in Table I. The adhesive/sealants are one-package silicone rubbers that cure on contact with atmospheric moisture. No composition data were obtained on these materials since they cure rapidly when exposed to air.

Preparation of Test Samples

Test samples of the silicone potting compounds were cast into shallow cups fabricated from aluminum foil. To ensure a uniform sample size, these cups were formed around a cylindrical glass template 3.0 cm in diameter. The cups were trimmed to a depth of 0.64 cm ($\frac{1}{4}$ -inch) and the sides of the cups reinforced with a thin strip of masking tape. Surface areas of the test specimens were calculated on the assumption that they were perfect cylinders having a surface area, $A = 2\pi r(r + h)$; r , the radius of the test specimen, and h , its height, were measured directly.

Test samples of the silicone adhesives were cast directly on strips of 11-mil Alclad 2024-T3 aluminum, 2.7 cm wide and 11 cm long, which had been degreased prior to use by wiping with chloroform. Surface areas were calculated directly from the measured length and width of the test specimen. An attempt was made to cast the silicone adhesives into cups, so that the data obtained for the adhesives would be comparable

with those for the potting compounds. It was found, however, that the silicone adhesives did not cure completely in thick sections.

In general, the silicone mixtures were prepared in the following manner. The required amount of Thermolite-12 catalyst (T-12) was added to 10 g of the silicone liquid or paste in a 50 ml beaker, and mixed thoroughly with a stainless steel spatula. This mixture was deaerated by placing it in a vacuum oven at room temperature and decreasing the pressure slowly to avoid spattering. When bubbles no longer rose to the surface (generally 15 to 20 min) the mixture was removed from the vacuum oven and poured gently into the aluminum foil cups to avoid air entrapment. The test samples were allowed to cure at room temperature for about 1 week before use. Relative humidity was not controlled unless otherwise noted. Details of the preparations of the various test specimens are given below.

RTV 11 and 60 - The silicone mixture was prepared by thoroughly mixing 10 g of the silicone liquid and 0.01 g (0.1% by weight) of T-12 in a small beaker. After deaeration, the mixture was poured into aluminum foil sample cups and allowed to cure for eight days at room temperature.

RTV 511 and 560 - The silicone mixture was prepared by thoroughly mixing 10 g of the silicone liquid and 0.02 g (0.2% by weight) T-12 in a small beaker. After deaeration the sample was cured for one week in a desiccator held at room temperature and 50% relative humidity.*

RTV 615 - The silicone mixture was prepared by thoroughly mixing 10 g of RTV 615 A with 1 g of RTV 615 B. After mixing and deaeration, the material was poured into aluminum cups and cured at room temperature for 7 days.

*50% relative humidity was maintained by filling the bottom section of the desiccator with a saturated solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

RTV Adhesive/Sealants (102, 106, 108, and 112) - All of these one-part materials were used directly from the tube and prepared in the same way, i.e., the material was spread with a spatula onto clean aluminum coupons to a thickness of approximately 10 mils and was cured for one week at room temperature and 50% relative humidity.*

Equipment

The vacuum system (Fig. 1) which utilizes a mechanical roughing pump (capacity, 140 liters per minute) and a mercury diffusion pump, can achieve routine pressures of $1-3 \times 10^{-6}$ mm Hg. Pressures were measured with an ion gauge (Consolidated Vacuum Corp.) calibrated for pressures of 0.025 mm to 10^{-7} mm Hg. The test specimens were placed in modified resin kettles (Fig. 2) which were heated by oil baths. The oil baths consisted of stainless steel beakers filled with Dow Silicone oil No. 550 and heated by resin kettle heating mantles. The bath temperatures were controlled by Thermistemp temperature controllers (Yellow Springs Instrument Co., Model 63RA), and the power to the heating mantles was supplied by a variable transformer. This arrangement maintained the oil baths at $\pm 2^{\circ}\text{C}$ of the desired temperature. In general the bath temperatures were held about five degrees higher to maintain the desired sample temperature. The temperature of the oil baths was measured directly by a mercury thermometer suspended in the bath; the temperature inside the resin pot was determined from a thermocouple wire inserted into the thermocouple tube which extended into the resin pot. Temperature measurements were made using a Leeds and Northrup temperature potentiometer which read directly in degrees centigrade. (Measurements were accurate to approximately $\pm 0.5^{\circ}\text{C}$.) The resin pot led directly to a conventional trap cooled with liquid nitrogen which could be isolated from the rest of the system so that its contents could be transferred into a glass sample bulb suitable for analytical techniques such as infrared, mass spectrometry, etc.

To determine weight loss, the test specimens were removed from the system and weighed on a Mettler "H" balance, accurate to ± 0.05 mg. Although continuous weighing under vacuum is recognized as a superior method, the present system can accommodate four different samples at one time, and thus permits rapid screening of materials as requested by JPL in this project.

Thermal Vacuum Testing Procedure

Each cured RTV potting compound was removed from its aluminum cup and weighed to the nearest 0.01 mg before testing; the adhesive/sealants were left on the aluminum strips, which had been weighed prior to coating. The RTV silicone samples were then tested at 150°C and approximately 5×10^{-6} mm Hg for total exposures of 150-200 hours. At approximately 24-hour intervals, the samples were removed for weighing. The temperature of the oil bath and of the interior of the resin pot, as well as the pressure of the system, were recorded at this time. The samples were removed from the resin pot with forceps and allowed to cool, then weighed to the nearest 0.01 mg, and returned to the system, which was immediately re-evacuated and the testing continued.

The following raw data were recorded for each test: (1) initial weight and dimensions of the cured test specimens; (2) weight of the test specimens to the nearest 0.01 mg at 24-hour intervals; (3) temperature of the system; (4) any changes in color or other physical properties of the sample; and (5) observations relating to outgassed materials, such as condensable oils on the inside of the head of the resin pot, above the level of heating. Note: if enough of the oil had evolved, an IR spectrum of the material was obtained with a Perkin-Elmer 221 Infrared Spectrophotometer.

Modification of Curing Processes

Postcuring of silicone samples was performed in a forced draft oven at 150°C for 24 hours (as recommended by GE for thick samples).

Vacuum postcuring of silicone samples was performed in the same vacuum system used in sample testing. Postcures were made at 150°C and 10^{-4} mm for a duration of 24-hours. Samples were stored in air for two days before thermal vacuum testing.

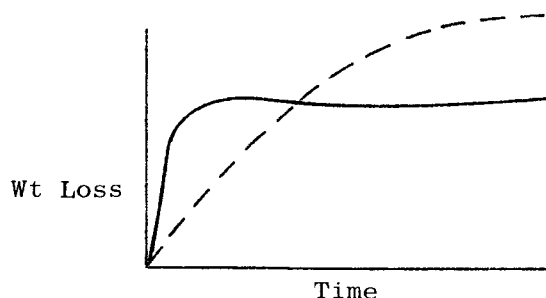
The effect of a higher level of curing agent in several of the RTV silicone resins was examined. The weight percent of T-12 and RTV silicones was raised from 0.1 - 0.2% to 0.5%, the maximum catalyst content recommended by GE and the samples were cured in the usual way.

RESULTS

The silicone materials examined in this study are listed in Table I along with the size and weight of the sample tested.

In general, the weight loss of heterogeneous materials under vacuum is dependent on temperature, on the amount and type of volatile materials present in the sample, and on the geometry of the test specimen. Because of the sensitivity to sample size and geometry, weight losses are reported both as percent (of total sample weight) and as absolute weight loss per unit surface area of the test specimen (g cm^{-2}). The change in weight loss with surface area is not well defined, and normalization of weight losses to a fixed sample size is not feasible. This situation is complicated further by the presence of two separate processes in weight loss measurements. The first is the desorption of surface contaminants, such as water and CO_2 ; the second is the outgassing of volatile materials entrained within the test specimen, such as solvents and unreacted material. If the amount of surface contamination is large compared with the amount of material diffusing from within the test specimen and if diffusion is comparatively slow, the weight loss curves for heterogeneous materials will be of the form shown in the

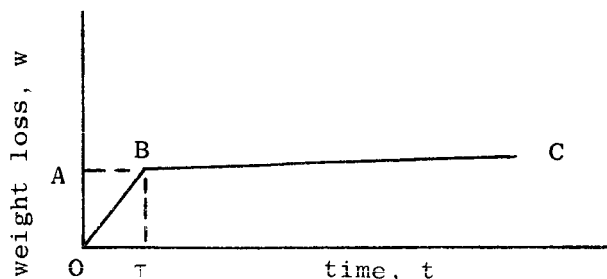
figure below (solid line).



If, on the other hand, the weight loss is primarily from the diffusion of material from within the test specimen, the shape of the weight loss curve will approach the logarithmic form characteristic of diffusion processes (dashed line). The RTV silicones, cured as recommended by the manufacturer, evolve rather large quantities of low molecular weight silicone oils. For this reason the form of the weight loss curves falls between those shown above. This is reflected in the long time required for the weight losses of these materials to become linear, i.e., to achieve a steady state. After about 100 hours, however, a good linear relationship is obtained, and treatment of data according to the two-part curve is adequate.

The results of outgassing studies on the RTV silicones are best presented in both tabular and graphical form. Two weight-loss curves are provided for each material tested; one curve shows the weight losses as percentages, the other shows weight losses in $\text{g cm}^{-2} \times 10^4$. From these curves, several parameters are estimated graphically.

If the plot of material loss versus time is assumed to have the form:



1. Steady State (SS) is represented by the linear portion (BC) of the curve.
2. Initial Weight Loss is the zero-time intercept of the linear portion of the weight loss curve (A).
3. Time until Steady State is the time required before the weight loss becomes linear (τ).
4. Steady State Loss Rate is given by the slope of the linear portion of the weight loss curve ($\Delta W/\Delta t$).

These parameters are extremely useful in summarizing the performance of a material under thermal vacuum conditions, and are included in tables following each graph. In addition, the outgassing characteristics of several of the RTV silicones have been plotted as a pure diffusion process (full logarithmic) for comparison. It will be noted that where the weight losses are large, e.g., RTV 511 and 560, the outgassing is almost entirely a diffusion effect; where the weight losses are smaller, surface effects become important and a linear relationship is no longer observed.

It is interesting to note that, despite the large weight losses of the silicone materials, none of the samples tested exhibited any color changes or noticeable alterations in physical properties.

The weight loss curves of the RTV potting compounds are shown in Figs. 3 and 4. In Fig. 5, the absolute weight loss per cm^2 of surface area is plotted logarithmically as mentioned above. Table II includes the weight loss parameters as defined above for these materials. The parameters have been calculated on a least squares basis assuming linearity after 100 hours. The times to steady state are, of course, approximate.

The weight loss data on the RTV adhesives are not directly comparable with those on the potting compounds. For this reason the data on the adhesives are treated separately. Figures 6 and 7 show the weight loss curves of these materials; Table III summarizes the weight loss parameters.

The weight loss curves of four RTV potting compounds that were postcured at 150°C for 24 hours in air before thermal vacuum testing was performed are shown in Fig. 8 and summarized in Table IV. Comparison of these curves with those for the same materials not postcured (Fig. 4) shows that weight losses have been reduced by about 50%. This treatment was not satisfactory because condensable oils still evolved during thermal vacuum testing.

No long term quantitative data are reported on the results of raising the curing agent content of the RTV silicone materials to 0.5%. Only a few hours after testing was begun, it was observed that large amounts of oil evolved from the test specimens and weight losses after 24 hours were found to be almost identical with those of the samples containing a lower level of catalyst. It was obvious that this modification was completely unsatisfactory, and thermal vacuum testing was discontinued after only 48 hours.

As the oil observed in these experiments could not be eliminated chemically, i.e., by methods designed to ensure better cure, it was necessary to remove it physically; the obvious means for this was by subjecting the test specimens to thermal vacuum treatment for 24-hours before testing. Considerable oil evolution took place during the first few hours of the thermal vacuum postcure, but this appeared to stop within 24-hours. These samples were allowed to stand in air for three days to re-adsorb surface contaminants so that they would be comparable to the other samples, then they were thermal vacuum tested in the usual way. This treatment was quite successful, as may be seen from Fig. 9 and Tables V and VI. Not only were all weight losses greatly reduced, but the volatile condensable oil had been eliminated. Figure 10 shows weight loss curves of RTV 60 for each type of treatment; the thermal vacuum or "space" postcuring is the most effective. It is realized, however, that this method might not be feasible for many applications of the RTV silicone materials.

Identification of Condensable Oil from Silicone Potting Compounds

As mentioned previously, large amounts of a clear, straw-colored oil were evolved from the silicone potting compounds during testing at 150°C and 10⁻⁶ mm Hg. Evolution of this oil began when the bath temperature reached 130-140°C and apparently continued for several hours. In the case of RTV 511, enough of this outgassed oil was available for an IR spectrum. (A drop of oil was placed between two NaCl discs, and the infrared spectrum recorded on a Perkin-Elmer 221 Spectrophotometer.) This spectrum was identical to that of RTV 511 indicating that the oil is low molecular weight siloxane of similar structure. IR spectra are shown in Fig. 11. It was originally felt that these oils were unreacted silicone fragments and an attempt was made to eliminate them by increasing the catalyst level in the silicone mixtures. This treatment was not effective as indicated above. Thin film studies were then made and these data showed no structural changes occurred in the infrared spectra of the RTV silicones heated at 150°C under vacuum for several hundred hours; therefore these oils are not degradation products. It was concluded on the basis of these data and our formulation experience that these oils were low molecular weight silicones, added in formulation, to serve as plasticizers and viscosity controllers.* They are of the same type as the silicone, i.e., dimethyl silicone oils in the case of dimethyl silicones, and phenyl-methyl for the phenyl-methyl based silicones.

*This is consistent with the fact that the low molecular weight oils are added to reduce viscosity, high weight losses were observed for the lower viscosity materials.

Table I
GENERAL ELECTRIC RTV SILICONES

Potting Compounds	Siloxane Base	Filler	Catalyst	Cured Silicone weight (g)	Test Sample area (cm ²)
RTV 11	Dimethyl	Silica or T ₁ O ₂	T-12 ¹	5.61986	21.1
RTV 60	Dimethyl	Iron Oxide	T-12	6.08525	20.1
RTV 511	Methyl-phenyl	Silica or T ₁ O ₂	T-12	4.98969	20.2
RTV 560	Methyl-phenyl	Iron Oxide	T-12	6.11943	22.0
RTV 615	Dimethyl	None	615 B ²	5.26418	22.7
<u>Adhesives³</u>					
RTV 102		white	one-part	0.46061	19.9
RTV 106		red	one-part	0.29606	20.8
RTV 108		translucent	one-part	0.40558	20.5
RTV 112		white	one-part	0.57201	20.5

¹Thermolite 12, i.e., dibutyl tin dilaurate.

²RTV 615 is composed of a part A which is siloxane base and a part B which is a catalyst (a proprietary material supplied by manufacturer).

³Appear to be dimethyl siloxanes.

Table II

WEIGHT LOSS PARAMETERS OF RTV SILICONE POTTING COMPOUNDS
(150°C and 5×10^{-6} mm Hg)

RTV Material	Initial Weight Loss		Weight Loss Rate		Est. time to steady state hrs
	$\text{g cm}^{-2} \times 10^4$	percent	$\text{g cm}^{-2} \text{ hr}^{-1} \times 10^6$	%/100 hr	
511	107	4.33	5.2	0.21	75
560	93.4	3.36	2.7	0.10	35
11	72.5	2.72	4.8	0.18	55
615	44.8	1.93	4.2	0.18	70
60	49.0	1.62	1.7	0.06	55

Table III

WEIGHT LOSS PARAMETERS OF RTV SILICONE ADHESIVE SEALANTS
(150°C and 5×10^{-6} mm Hg)

RTV Material	Initial Weight Loss		Weight Loss Rate		Est. time to steady state hrs
	$\text{g cm}^{-2} \times 10^4$	percent	$\text{g cm}^{-2} \text{ hr}^{-1} \times 10^6$	%/100 hr	
112	14.0	6.07	0.1	0.07	100
108	11.8	5.90	0.1	0.11	100
106	7.4	5.42	0.3	0.09	100
102	16.8	5.95	0.1	0.05	100

Table IV

WEIGHT LOSS PARAMETERS OF SELECTED POSTCURED SILICONES
(150°C and 5×10^{-6} mm Hg)

Silicone	Initial Weight Loss		Weight Loss Rates		Est. time to steady state
	$\text{g cm}^{-2} \times 10^4$	percent	$\text{g cm}^{-2} \text{ hr}^{-1} \times 10^6$	%/100 hr	
60	20.7	0.82	0.8	0.04	80
11	26.6	1.21	2.6	0.21	80
560	50.0	1.71	1.0	0.03	95
511	47.1	1.88	2.8	0.16	100

Table V

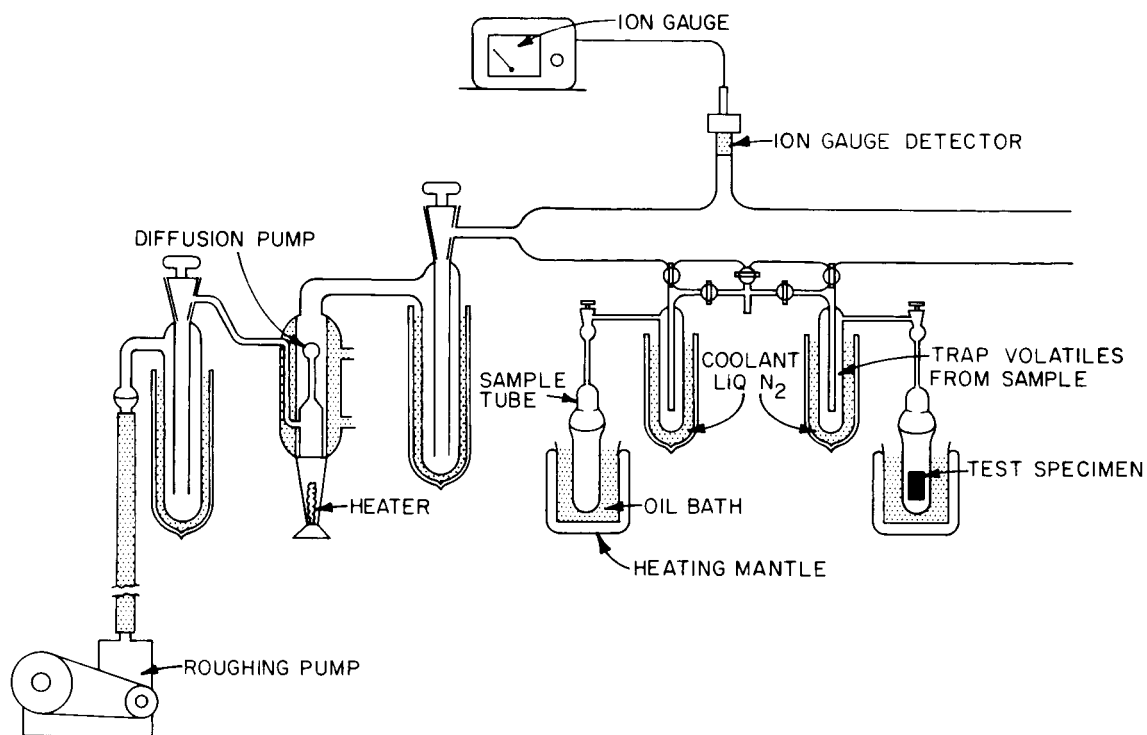
WEIGHT LOSS PARAMETERS OF SELECTED VACUUM POSTCURED RTV SILICONES
(150°C and 5×10^{-6} mm Hg)

Silicone	Initial Weight Loss		Weight Loss Rates	
	$\text{g cm}^{-2} \times 10^4$	percent	$\text{g cm}^{-2} \text{ hr}^{-1} \times 10^6$	%/100 hr
RTV 60	10.4	0.35	0.0	0.01
RTV 560	11.3	0.46	0.2	0.01
RTV 11	14.1	0.52	3.3	0.11
RTV 615	17.9	0.78	0.8	0.10

Table VI

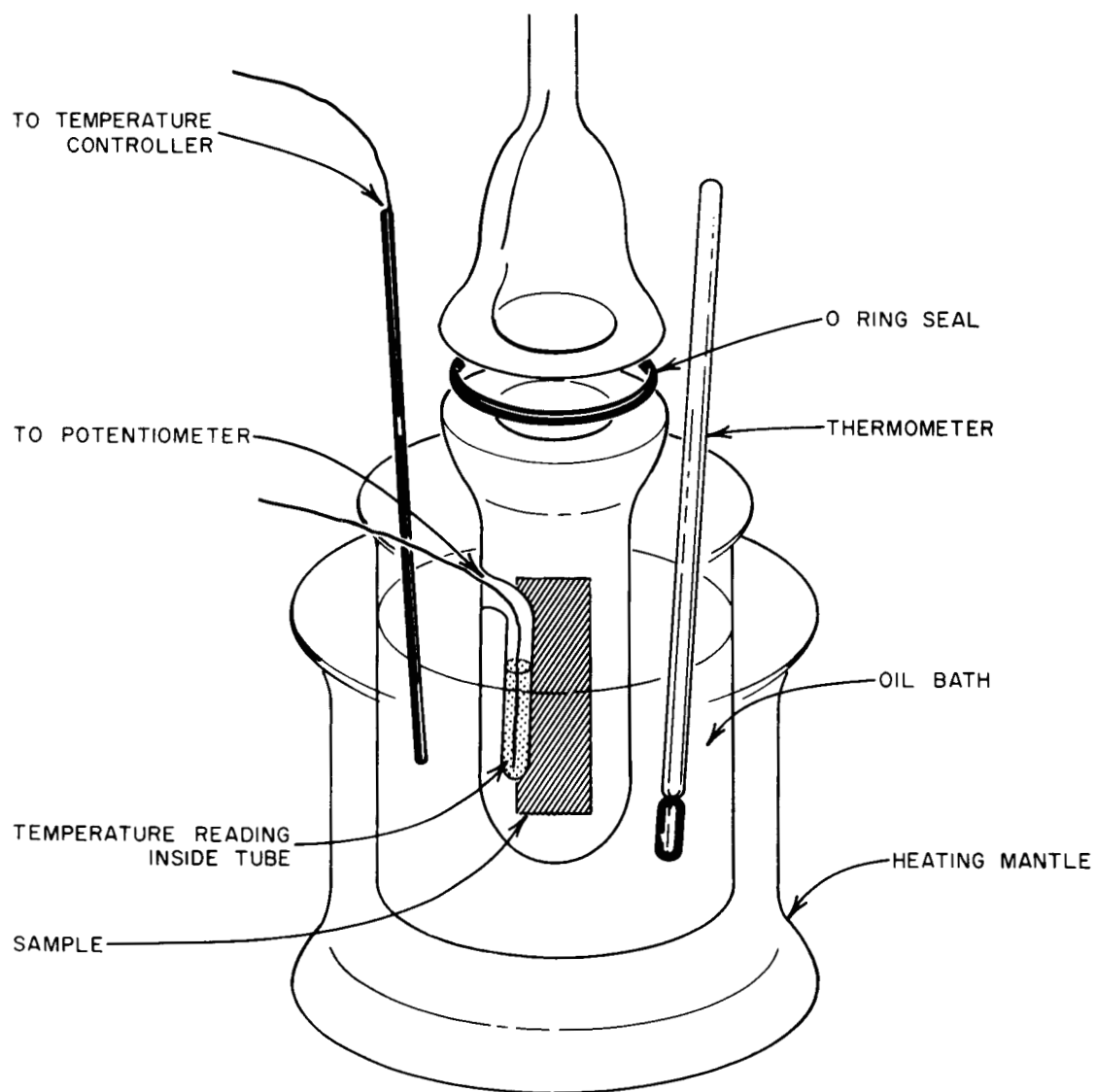
WEIGHT CHANGES DURING VACUUM POSTCURE CYCLE

Silicone RTV	Original Wt. untreated sample	Weight after post- curing	% wt Lost	Wt after 3 days in air	% wt Gained	Over-all wt. loss %
615	4.68625	4.61465	1.53	4.61595	0.03	1.50
11	5.68011	5.61990	1.06	5.62569	0.08 ₅	0.97 ₅
60	5.65682	5.59112	1.16	5.59573	0.08	1.08
560	4.61445	4.47032	3.12	4.47225	0.06	3.06



TA-5046-4

FIG. 1 COMPLETE VACUUM APPARATUS FOR THERMAL-VACUUM TREATMENT



TA-5046-5

FIG. 2 DETAILED DRAWING OF SAMPLE CELL ASSEMBLY

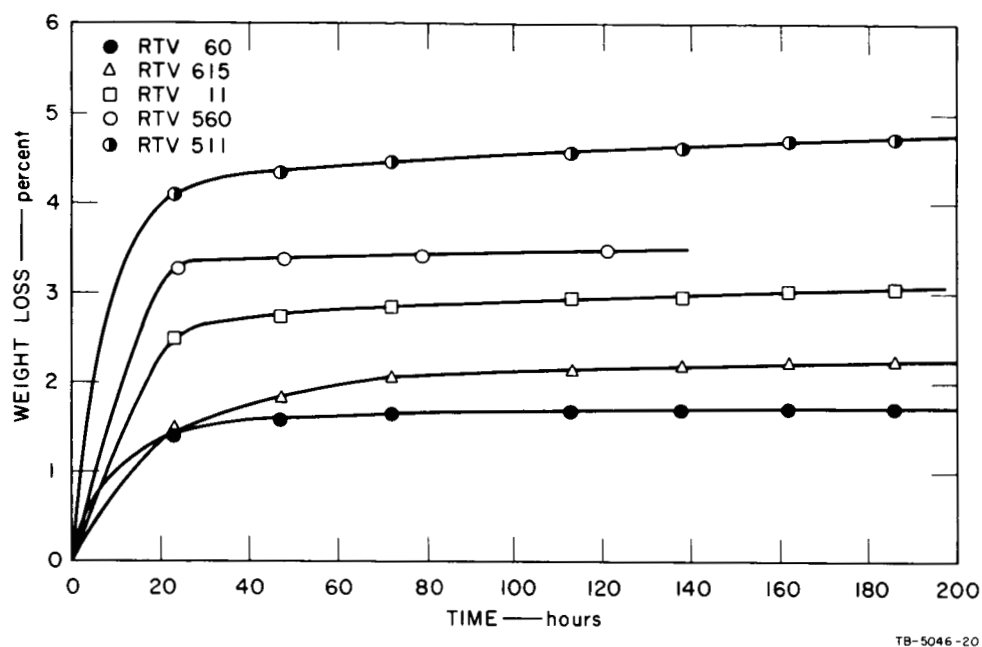
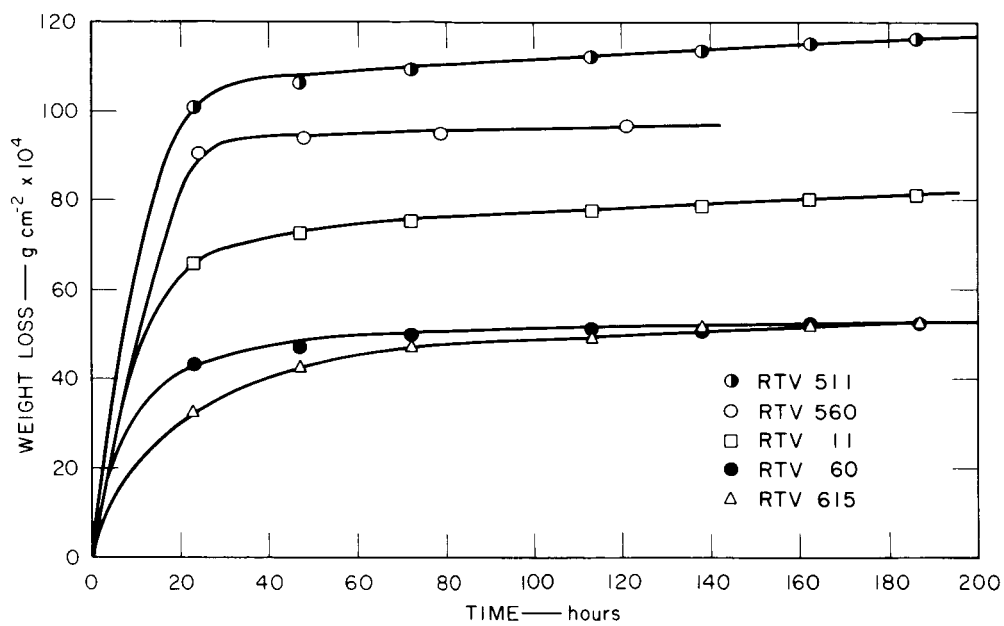
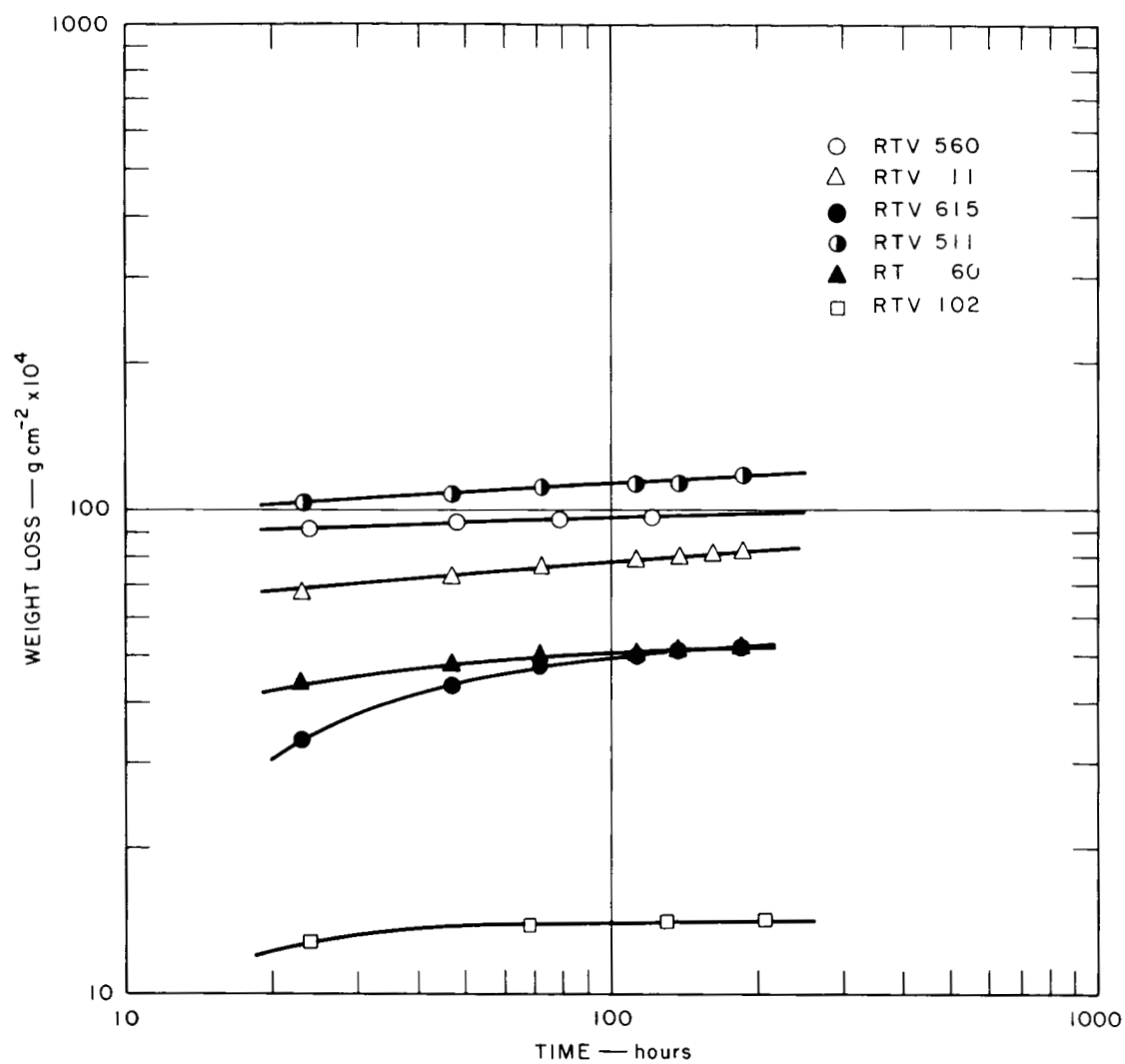


FIG. 3 PERCENT WEIGHT LOSS OF RTV SILICONE POTTING COMPOUNDS
AT 150°C AND 5×10^{-6} mm Hg



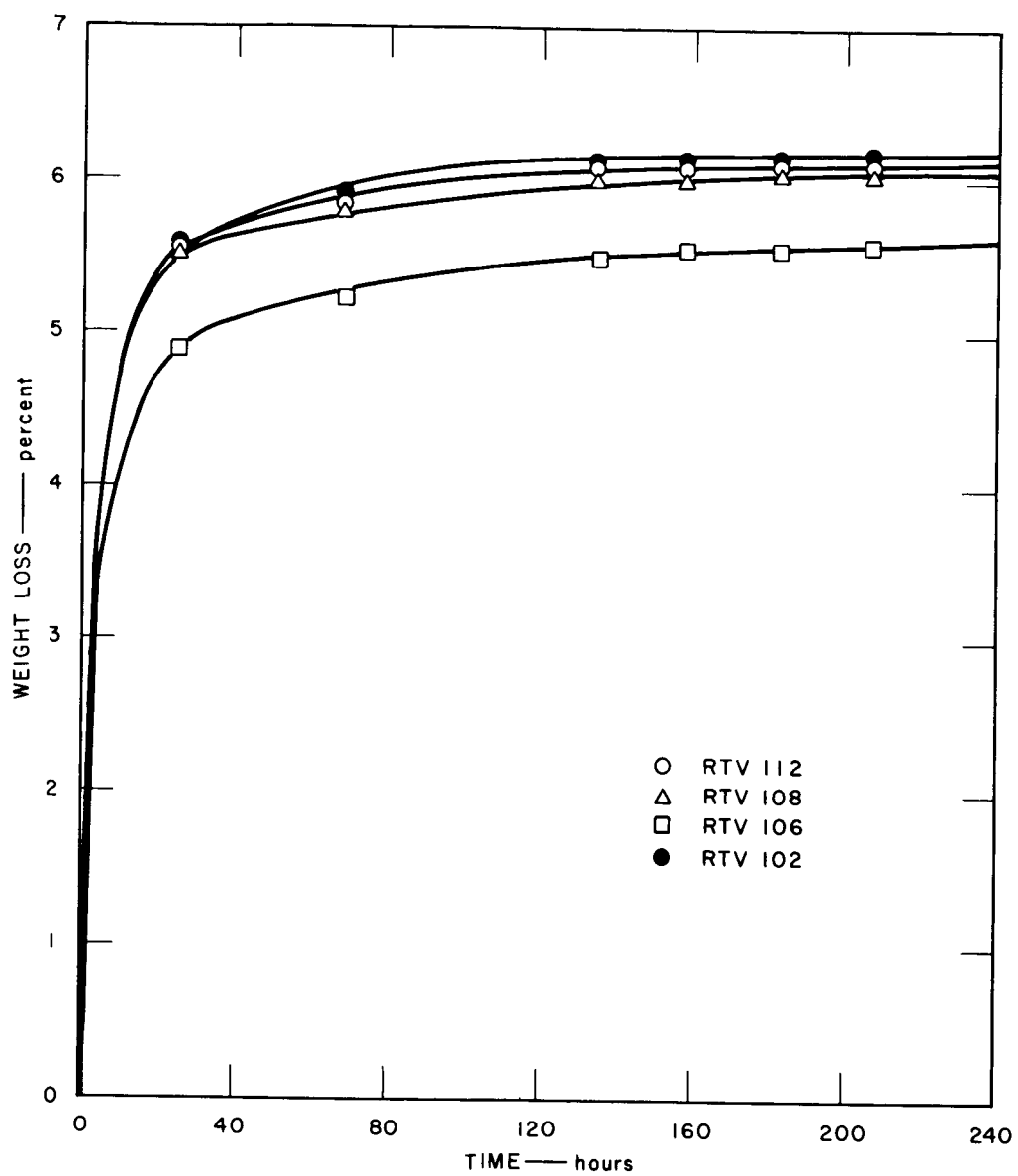
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FIG. 4 WEIGHT LOSS PER UNIT SURFACE AREA OF RTV SILICONE
POTTING COMPOUNDS AT 150°C AND 5×10^{-6} mm Hg



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FIG. 5 WEIGHT LOSS PER UNIT SURFACE AREA OF RTV SILICONE COMPOUNDS AT 150°C AND 5×10^{-6} mm Hg, AS AN EXPONENTIAL FUNCTION OF EXPOSURE TIME



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FIG. 6 PERCENT WEIGHT LOSS OF RTV SILICONE ADHESIVE/SEALANTS
AT 150°C AND 5×10^{-6} mm Hg

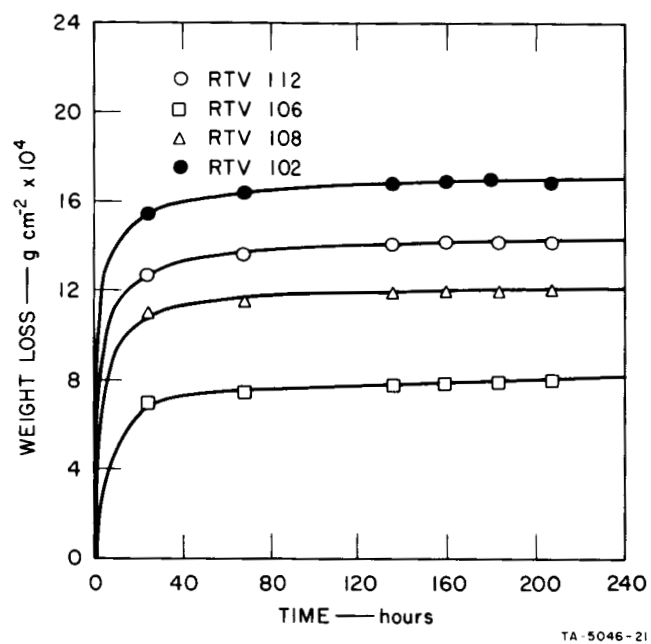
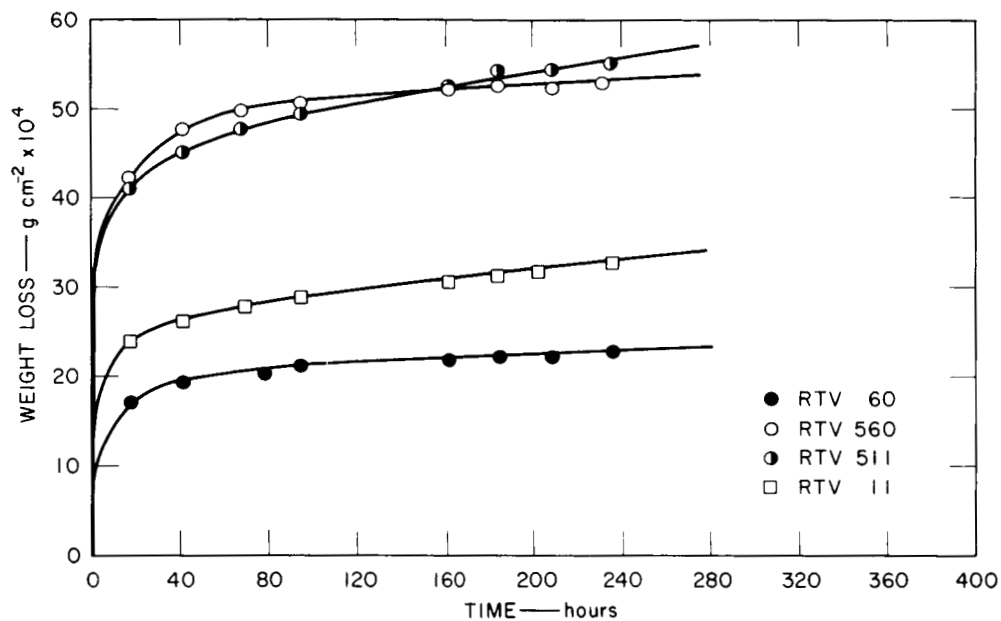
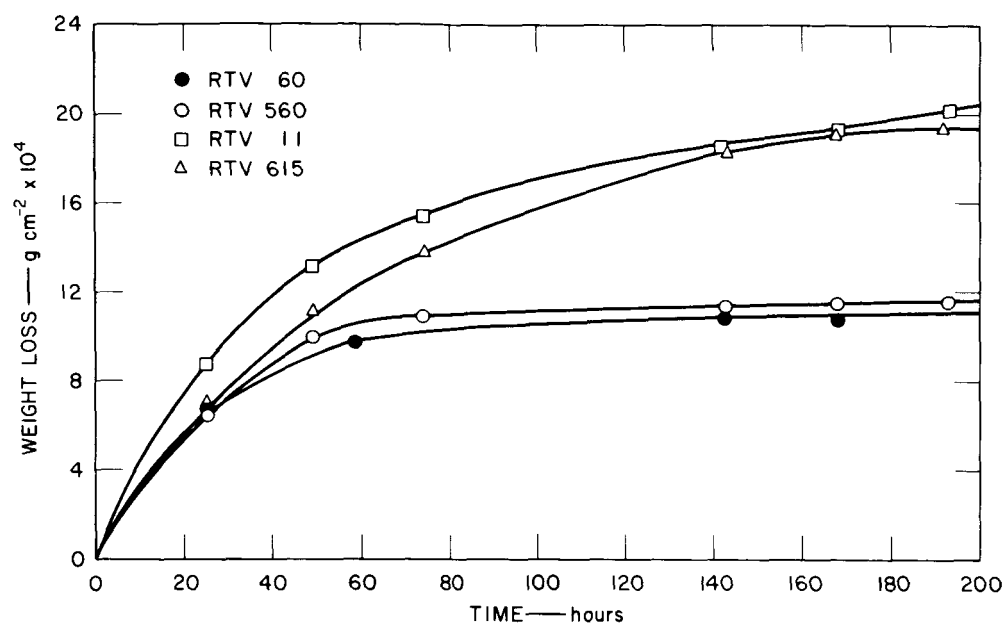


FIG. 7 WEIGHT LOSS PER UNIT SURFACE AREA OF RTV SILICONE ADHESIVE/SEALANTS AT 150°C AND 5×10^{-6} mm Hg



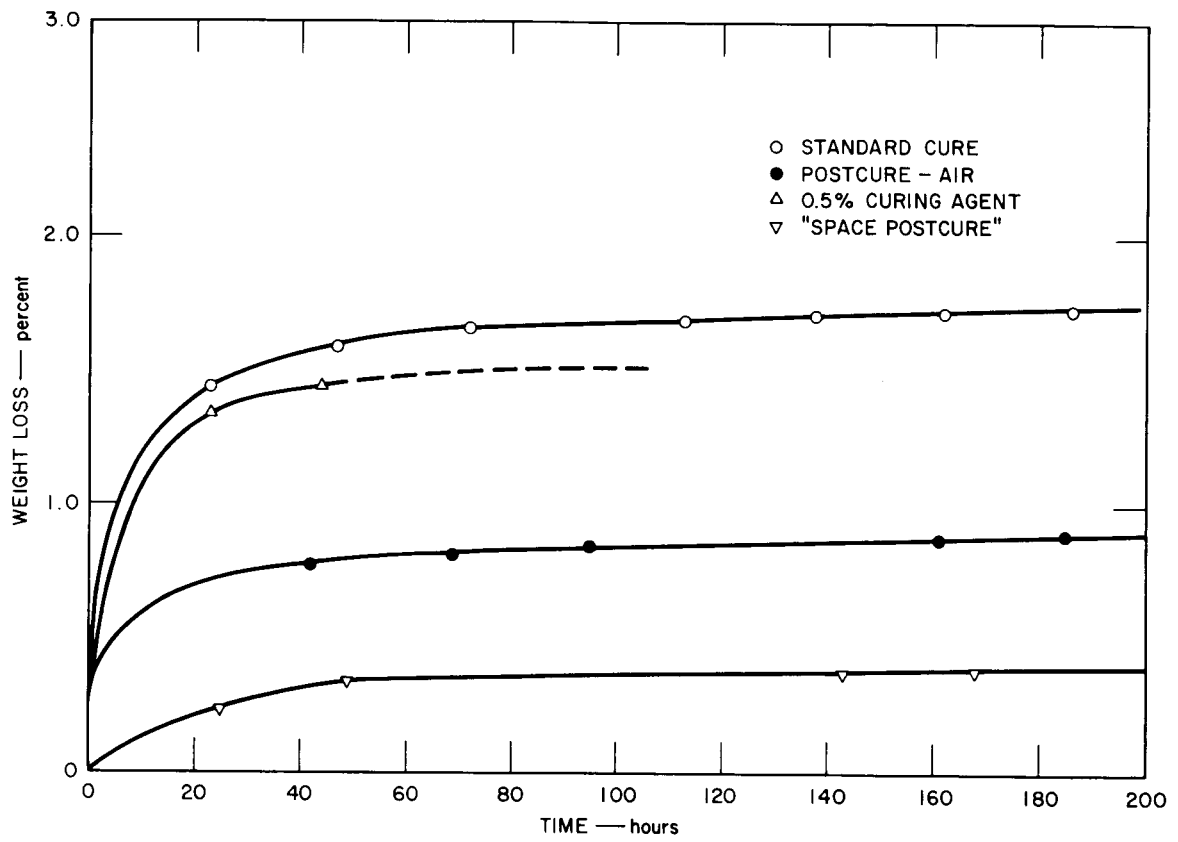
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FIG. 8 WEIGHT LOSS PER UNIT SURFACE AREA OF SEVERAL RTV SILICONE POTTING COMPOUNDS AT 150°C AND 5×10^{-6} mm Hg AFTER POSTCURING FOR 24 HOURS IN AIR AT 150°C



TB-5046-17

FIG. 9 WEIGHT LOSS PER UNIT SURFACE AREA OF SEVERAL RTV SILICONE POTTING COMPOUNDS AT 150°C AND 5×10^{-6} mm Hg AFTER POSTCURING FOR 24 HOURS *in vacuo* AT 150°C



TB-5046-2

FIG. 10 EFFECT OF VARIOUS PRETREATMENTS ON THE OUTGASSING CHARACTERISTICS OF RTV 60 AT 150°C AND 5×10^{-6} mm Hg

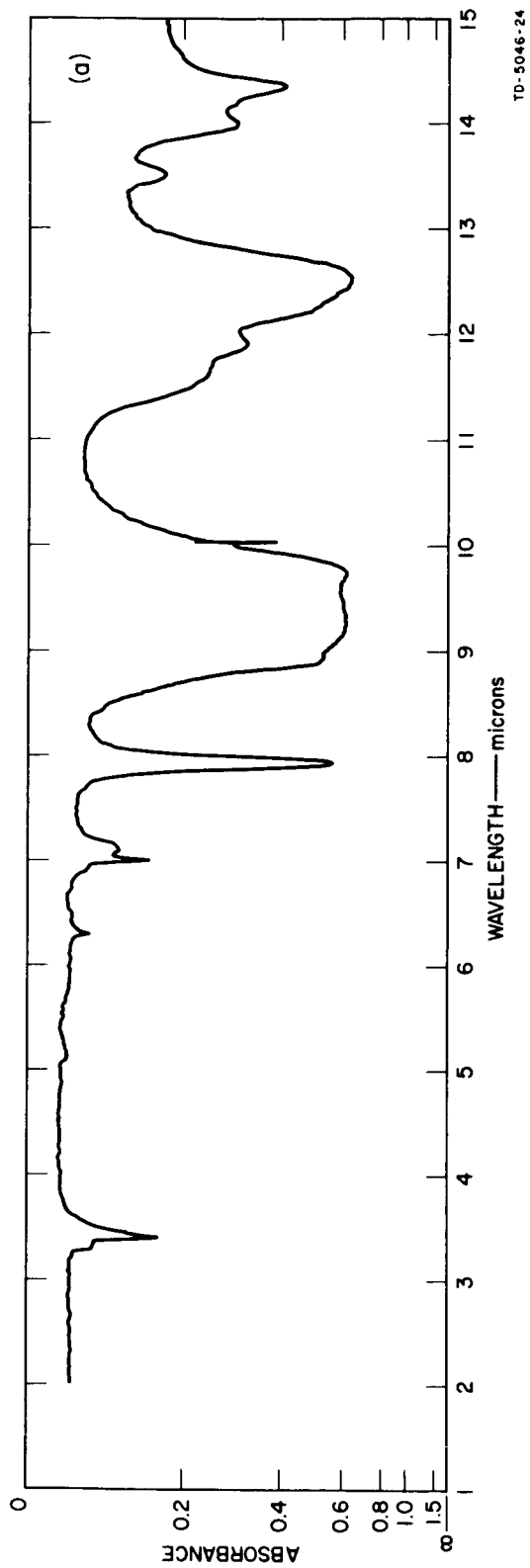


FIG. 11(a) INFRARED SPECTRUM OF RTV 511 FILM AFTER REMOVAL OF FILLER

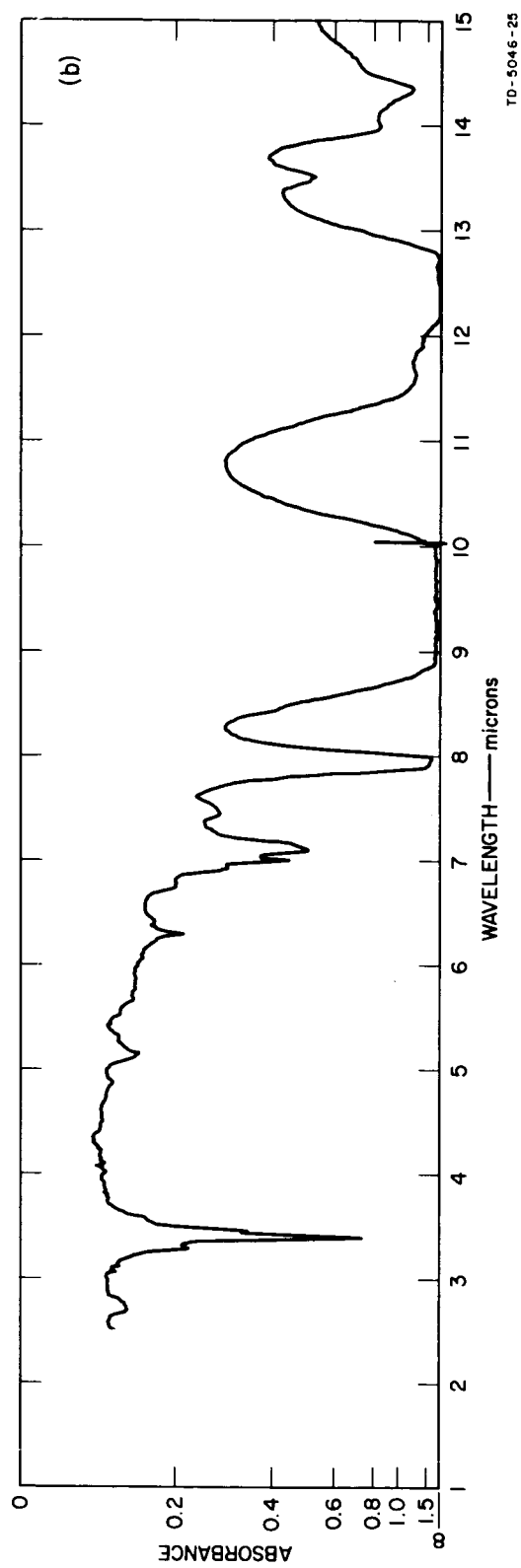


FIG. 11(b) INFRARED SPECTRUM OF OIL EVOLVED FROM AN RTV 511 TEST SAMPLE AT 150°C AND 5×10^{-6} mm Hg

DISCUSSION

Silicone rubbers have found wide application in spacecraft both as adhesives and as potting compounds. Their usefulness is based primarily on their excellent thermal stability; commercial materials in vacuo are stable to approximately 200°C and very pure siloxane polymers may be stable to 400°C. A brief discussion of the chemistry of silicone polymers will be found in Appendix A. It is immediately clear that material degradation is not an important factor in determining the thermal vacuum properties of these materials at 150°C.

Despite this, all five RTV silicone potting compounds, RTV 60, 11, 560, 511, and 615 performed poorly under thermal vacuum conditions--large amounts of condensable oils evolved. The outgassing characteristics of these materials are shown in Figs. 3 and 4, and summarized in Table III; 40-80 hours were required to achieve a steady state; initial weight losses ranged from 1.6-4.3% and rates were of the order of 0.1-0.2% per hundred hours.

These large weight losses led us to question whether these materials were completely cured. The test specimens employed in this study were relatively thick, on the order of $\frac{1}{4}$ inch. For samples of $\frac{1}{4}$ inch or more in thickness, the manufacturer recommends heating the material to service temperature to speed up the cure.* For this reason, several of the RTV silicone potting compound test specimens were postcured for 24 hours at service temperature (150°C) before they underwent thermal vacuum testing. It was found that these materials gave somewhat better performance than those which had been cured at room temperature only. Weight losses decreased about fifty percent, but this pretreatment did not prevent the evolution of rather large amounts of low molecular weight silicone oil.

*GE Technical Data Book, S-3B, Page 10.

Because of the thickness of the test specimens, minimum amounts of the catalyst (T-12) had been employed in preparing the silicone mixtures, as recommended by the manufacturer. T-12 is considered a very reliable catalyst, but it was of interest to see if a more complete cure could be obtained by using a larger amount in formulating the test specimens. Therefore, the catalyst level in several potting compounds was raised from the 0.1-0.2% range to 0.5%.* It was found that this had virtually no effect on the thermal vacuum behavior of the silicone potting compounds, and after 48 hours testing, this approach was abandoned.

It was apparent from these postcuring studies that, although improved outgassing characteristics were obtained, the outgassing of the oils was not eliminated. When it was concluded that these oils were additives which could not be expected to cure into the siloxane network, a thermal vacuum postcure treatment was undertaken and produced excellent results. The outgassing of oil was completely eliminated, and the outgassing parameters were low, i.e., initial weight losses of less than 1% and rates of 0.01 to 0.1% per hundred hours.

It was found that the percent weight losses of the Adhesive/Sealants, RTV 102, 108, and 112 were very similar; all had initial weight losses of about 6.0%, and all evolved oils within the first hour of heating. RTV 106 is a silicone adhesive intended for high temperature use, and therefore it is not surprising that its thermal vacuum properties were superior to the others.

Because of the difficulty encountered in obtaining reliable or meaningful mass spectroscopy data on the outgassed volatiles in the thermal vacuum studies of epoxide adhesives, no such analyses were attempted for the RTV silicone rubbers. It is easy to predict, however

*This is the maximum amount suggested by GE.

what volatile materials may be expected from these materials. The major product (low molecular weight silicone oils), has been extensively discussed elsewhere in this report. Although the manufacturer states that the uncured RTV silicone rubber potting compounds are 100% solids, this is not true of the cured materials. Reference to the crosslinking mechanism of RTV silicones (see Appendix A, reaction I) shows that each crosslink formed results in two moles of alcohol (generally methanol) which is very volatile and should present no difficulties. Most of this alcohol may be expected to evaporate during the cure cycle, and if elevated temperatures are employed in curing, it should disappear altogether. Volatiles formed in the curing of the Adhesive/Sealants (Appendix A, reaction II) present a more serious problem. These materials cure with the evolution of acetic acid, which is less volatile. It is advisable, then, that all Adhesive/Sealants receive some treatment before use in spacecraft.

It is necessary that all the silicone materials tested in this study be subjected to some modification of posttreatment or formulation that will eliminate the outgassing of low molecular weight silicone oils. Although the vacuum postcuring technique was quite successful in eliminating these oils, it is realized that this treatment might not be feasible for many spacecraft assemblies. For some uses a more suitable method might be changes in resin formulation which would involve, for example, an alternative means of viscosity control.

CONCLUSIONS

It has been found that all the RTV silicone compounds tested in this study are unsuitable for spacecraft use when cured as recommended by the manufacturer, due to the large amounts of low molecular weight silicone oil evolved under simulated space conditions. Attempts to eliminate this oil by postcuring in air at service temperature and by increasing the amounts of curing agent in the resin were not successful since oil was still evolved from the test specimens.

It was found that this volatile, condensable oil may be removed from a silicone rubber by heating the rubber to 150°C at about 10^{-4} mm Hg for 24 hours; this treatment greatly improved the outgassing characteristics of the silicone materials. It is realized, however, that this treatment may not be feasible for all spacecraft applications of the silicone rubbers.

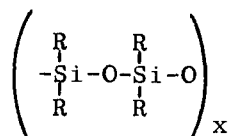
ACKNOWLEDGMENT

The authors wish to thank Mrs. Marijane Hoover for preparing the RTV Silicone test specimens used in this study and Dr. M. A. Golub for helpful discussions on these materials.

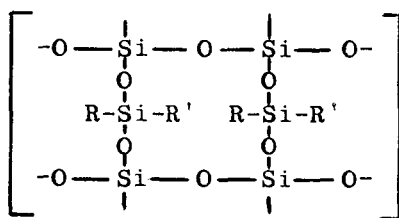
APPENDIX A

CHEMISTRY OF (POLY)SILOXANES

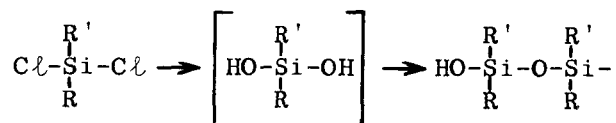
The silicone polymers discussed in this report are based on the polymeric siloxane structure



Where R is either phenyl or methyl. The linear poly siloxanes are fluids to gums depending on their molecular weight, and may be crosslinked under certain conditions to form a polymer network of the form



The intermediate in the formation of the siloxanes is the hydroxy silane, formed by hydrolysis of the corresponding chlorosilane.

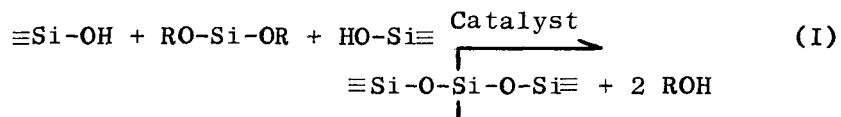


The materials discussed in this report all have methyl as the R group; R' may be either another methyl, as is the case for RTV 60 or 11, or it may be phenyl, as for RTV 511 or 560. The phenyl and methyl silicones have a number of properties which render them especially suitable for commercial applications. Of particular interest for space application is their high heat stability, accompanied by retention of physical properties, such as flexibility, over a broad temperature range (-70° to 250°C). They are also chemically inert and very stable toward oxidation.

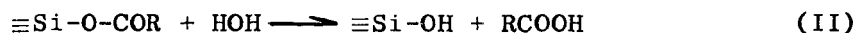
The silicone rubbers are crosslinked structures. The silicone

preparation obtained from the manufacturer consists of a mixture of long chain siloxane gum, an inorganic filler, and an oxidizing agent or catalyst. Dibutyl tin dilaurate was employed in all studies reported above.

In the room temperature cured materials, crosslinking takes place between the hydroxy silane chain ends and alkoxy groups on a crosslinking agent:



A second type of room temperature cured rubber is kept in a closed container such as a tube until used. On exposure to atmospheric moisture the rubber cures, as a result of hydrolysis of the acetyloxy groups.



The hydroxyl group is then available for crosslinking. The one-part Adhesive/Sealants, RTV 102, 106, 108, and 112 are undoubtedly of this type.

Under high vacuum, the pure siloxane polymer is stable to 350-400°C; at higher temperatures the Si-O bonds are broken and reform as volatile, low molecular weight fragments. In commercial silicones the degradation temperature is much lower, primarily because of the presence of impurities in the polymer. In practice it has been found that thermal stability is also sensitive to moisture, oxygen, and oxidants, as well as trace impurities.